

Implementation of Z-vector method in the relativistic coupled cluster framework to calculate first order energy derivatives: Application to SrF molecule

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The molecular dipole moment and magnetic hyperfine structure constant demand an accurate wavefunction far from the nucleus and in near nuclear region, respectively. We, therefore, employ the so-called Z-vector method in the domain of relativistic coupled cluster theory to calculate the first order property of molecular systems in their open-shell ground state configuration. The implemented method is applied to calculate molecular dipole moment and parallel component of the magnetic hyperfine structure constant of SrF molecule. The results of our calculation are compared with the experimental and other available theoretically calculated values. We are successful in achieving good accordance with the experimental results. The result of our calculation of molecular dipole moment is in the accuracy of $\sim 0.5\%$, which is clearly an improvement over the previous calculation based on the expectation value method in the four component coupled cluster framework [V. S. Prasanna *et al*, Phys. Rev. A **90**, 052507 (2014)] and it is the best calculated value till date. Thus, it can be inferred that the Z-vector method can provide an accurate wavefunction in both near and far nuclear region, which is evident from our calculated results.

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Theoretical physicists find it very challenging to calculate the spectroscopic properties of atoms and molecules. The precise description of the spectroscopic properties demands the wavefunction to be accurate both in the nuclear region and the region far from the nucleus. The calculation of an accurate wavefunction involving heavy atoms and molecules needs to include the relativistic and electron correlation effects simultaneously, as these two effects are non-additive in nature [1, 2]. The best possible way to include the effects of relativity in a single determinantal theory is to solve the Dirac-Hartree-Fock (DHF) Hamiltonian in its four component formalism. The DHF Hamiltonian converts the complicated many electron problem into a sum of many one-electron problems by assuming an average electron-electron interaction. Therefore, the DHF Hamiltonian lacks the correlation of opposite spin electrons. The missing electron correlation can be included by adding orthogonal space to the DHF wavefunction. On the other hand, normal coupled cluster (NCC) [3–5] method is known to be the most elegant many-body theory to effectuate the dynamic part of the electron correlation.

The calculations of one electron response properties in the NCC framework, can either be done by taking expectation value of the desired property operator or as a derivative of energy. These two approaches are not same as the NCC is by nature non-variational. In fact, the first order derivative of energy is the corresponding expectation value plus some additional terms, which makes the derivative approach closer to the full configuration

interaction (FCI) property value. It is worth to mention that the expectation value approach in the NCC leads to a nonterminating series and any truncation scheme introduces an additional error [6].

In general, the energy is a function of both the determinantal coefficients (C_D) in the expansion of the many electron correlated wavefunction and the molecular orbital coefficients (C_M) for a fixed nuclear geometry. The first order energy derivative in NCC can be written as

$$\frac{\delta E[C_D(\lambda), C_M(\lambda)]}{\delta \lambda} = \frac{\delta E}{\delta C_D} \frac{\delta C_D}{\delta \lambda} + \frac{\delta E}{\delta C_M} \frac{\delta C_M}{\delta \lambda}.$$

Thus, for the calculation of energy derivative in NCC framework, it is, therefore, necessary to calculate the derivative of energy with respect the determinantal coefficients as well as the molecular orbital coefficients. It further requires the derivative of the determinantal coefficients and molecular orbital coefficients with respect to the external field of perturbation. However, Bartlett and co-workers [7] have shown that these derivative terms can be transformed into a single linear equation by using Z-vector method. The advantage of Z-vector method [8, 9] is that for the calculation of several properties, one needs to solve a single linear equation instead of solving equations for each external perturbation field of interest. The detailed diagrammatic of Z-vector method in NCC framework is given in Ref. [9].

In this rapid communication, we have shown that the Z-vector method in the NCC framework within its four component description can generate an accurate wavefunction in the near nuclear region as well as in the region far from the nucleus. To justify our argument, we have compared magnetic hyperfine structure constant (HFS) and molecular dipole moment of SrF with the experi-

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mental values as the calculation of these properties need an accurate wavefunction in the near nuclear region and the region far from the nucleus, respectively. The reason for choosing SrF molecule is as follows: The knowledge of long range dipole-dipole interaction is very important to produce ultracold molecules in optical lattice [10]. SrF molecule can be cooled by laser spectroscopy [11] and thus it can be used for high precession spectroscopy [12, 13]. Currently an experimental search for parity violation using SrF is in progress [14]. Therefore, detailed knowledge of the spectroscopic properties like dipole moment and magnetic HFS is very important to interpret the experimental findings.

The Many body time-independent Dirac-Coulomb Hamiltonian is given by

$$H = \sum_i \left[-c\vec{\alpha}_i \cdot \vec{\nabla}_i + (\beta - I)c^2 + \sum_A V_A^{nuc}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \right], \quad (1)$$

where c is the speed of light, α and β are the usual Dirac matrices, I is the 4×4 identity matrix. $V_A^{nuc}(r_i)$ is the nuclear potential term of nucleus A .

The dynamic part of the electron correlation is included using the coupled cluster method. The wave function in the coupled cluster method is defined as

$$|\Psi_{cc}\rangle = e^T |\Phi_0\rangle \quad (2)$$

where, $|\Phi_0\rangle$ is the ground state single determinant wavefunction and T is cluster operator which is given by

$$T = T_1 + T_2 + \dots + T_N = \sum_n T_n \quad (3)$$

with

$$T_m = \frac{1}{(m!)^2} \sum_{ij..ab..} t_{ij..}^{ab..} a_a^\dagger a_b^\dagger \dots a_j a_i \quad (4)$$

$i,j(a,b)$ are the hole(particle) indices and $t_{ij..}^{ab..}$ are the cluster amplitudes corresponding to the cluster operator T_m . The equations for n -body cluster amplitudes and correlation energy are given by

$$\langle \Phi_{i..}^{a..} | (H_N e^T)_C | \Phi_0 \rangle = 0 \quad (5)$$

$$\langle \Phi_0 | (H_N e^T)_C | \Phi_0 \rangle = E^{corr} \quad (6)$$

where H_N is the normal ordered Hamiltonian and the subscript C indicates only the connected terms in the contraction between H_N and T . The connectedness ensures size-extensivity. Once the cluster amplitude equation (5) is solved, the correlation energy can be obtained from equation 6. The coupled cluster energy is a function of both the determinantal coefficients (C_D) and the molecular orbital coefficients (C_M). Therefore, the calculation of coupled cluster energy derivative need both the derivative of C_D s and C_M s with respect to external

field of perturbation. However, the equations involving derivative of C_D s and C_M s are linear equations. Thus, one needs to solve the linear equations for each external field perturbation of interest. This can be avoided with the introduction of an antisymmetrized de-excitation operator, Λ , where the equations for the amplitudes of Λ is perturbation independent. Therefore, the solution of one linear equation is required instead of solving for each external perturbation. The second quantized form of the perturbation independent operator, Λ is given by

$$\Lambda = \Lambda_1 + \Lambda_2 + \dots + \Lambda_N = \sum_n \Lambda_n \quad (7)$$

where

$$\Lambda_m = \frac{1}{(m!)^2} \sum_{ij..ab..} \lambda_{ab..}^{ij..} a_i^\dagger a_j^\dagger \dots a_b a_a \quad (8)$$

where $i,j(a,b)$ are the hole(particle) indices and $\lambda_{ab..}^{ij..}$ are the cluster amplitudes corresponding to the cluster operator Λ_m . The detailed description of Λ operator and Λ amplitude equation is given in reference [9]. The working Λ amplitude equation is given by

$$\begin{aligned} \langle \Phi_0 | [\Lambda(H_N e^T)_C]_C | \Phi_{i..}^{a..} \rangle + \langle \Phi_0 | (H_N e^T)_C | \Phi_{int} \rangle \\ \langle \Phi_{int} | \Lambda | \Phi_{i..}^{a..} \rangle + \langle \Phi_0 | (H_N e^T)_C | \Phi_{i..}^{a..} \rangle = 0 \end{aligned} \quad (9)$$

where Φ_{int} is the determinant corresponding to the intermediate excitation between Φ_0 and $\Phi_{i..}^{a..}$. In the coupled cluster single and double (CCSD) model, Λ becomes, $\Lambda = \Lambda_1 + \Lambda_2$. The explicit equations for the amplitudes of Λ_1 and Λ_2 operators are

$$\langle \Phi_0 | [\Lambda(H_N e^T)_C]_C | \Phi_i^a \rangle + \langle \Phi_0 | (H_N e^T)_C | \Phi_i^a \rangle = 0, \quad (10)$$

$$\begin{aligned} \langle \Phi_0 | [\Lambda(H_N e^T)_C]_C | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_C | \Phi_i^a \rangle \\ \langle \Phi_i^a | \Lambda | \Phi_{ij}^{ab} \rangle + \langle \Phi_0 | (H_N e^T)_C | \Phi_{ij}^{ab} \rangle = 0. \end{aligned} \quad (11)$$

It is interesting to note that the term $\langle \Phi_0 | (H_N e^T)_C | \Phi_i^a \rangle \langle \Phi_i^a | \Lambda | \Phi_{ij}^{ab} \rangle$ of equation 11 yields one disconnected diagram, which is given in Fig. 1. The said diagram is not of the type of closed with disconnected part. This ensures that the energy derivative is

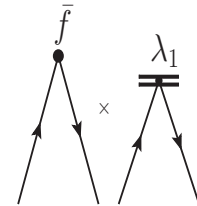


FIG. 1: Disconnected yet linked diagram in Λ_2 equation.

linked and thus size extensive. The equation for energy derivative can be written as

$$\Delta E' = \langle \Phi_0 | (O_N e^T)_C | \Phi_0 \rangle + \langle \Phi_0 | [\Lambda (O e^T)_C]_C | \Phi_0 \rangle \quad (12)$$

where O_N is the derivative of normal ordered perturbed Hamiltonian with respect to external field of perturbation.

The molecular dipole moment of a heavy diatomic molecule arises due to the fact that the nuclear charge of the two atoms are not same and thus the electron density is not evenly distributed around the two nucleus. In the Born-Oppenheimer approximation, we can separate out the nuclear and electronic contribution from the total contribution. The dipole moment operator is given by

$$\vec{\mu} = - \sum_i \vec{r}_i + \sum_A Z_A \vec{r}_A \quad (13)$$

where i stands for the electron and Z_A is the atomic number of nucleus A . The first term of the above equation is the electronic contribution and the second term is the nuclear contribution.

The magnetic HFS arises due to the interaction of nuclear magnetic dipole moment with the magnetic moment of electrons. Thus, the magnetic HFS is the sum of one body interactions from the point of view of electronic structure theory [2]. The magnetic vector potential (\vec{A}) at a distance \vec{r} is given by

$$\vec{A} = \frac{\vec{\mu}_k \times \vec{r}}{r^3}, \quad (14)$$

where $\vec{\mu}_k$ is the magnetic moment of the nucleus K . The perturbed HFS Hamiltonian of an atom due to \vec{A} in the Dirac theory is given by $H_{hyp} = \sum_i^n \vec{\alpha}_i \cdot \vec{A}_i$, where n is the total no of electrons and α_i denotes the Dirac α matrices for the i^{th} electron. The z projection (along the molecular axis) of the expectation value of the corresponding perturbed HFS Hamiltonian gives the parallel magnetic HFS constant, $A_{||}$, which is given by

$$A_{||} = \frac{\vec{\mu}_k}{I\Omega} \cdot \langle \Psi_\Omega | \sum_i^n \left(\frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right)_z | \Psi_\Omega \rangle, \quad (15)$$

where I is the nuclear spin quantum number and Ω represents the z component (along molecular axis) of the total angular momentum of the diatomic molecule.

The N electron ground and excited determinants are constructed with the one electron spinors, those are the solutions of Dirac-Hartree-Fock equation. The DIRAC10 [15] program package is used to solve the Dirac-Fock equation and to obtain the matrix elements required for property calculations. Gaussian charge distribution is considered as the nuclear model where the nuclear parameters [16] are taken as default values in DIRAC10. Large and small component basis functions are generated by applying restricted kinetic balance (RKB) [17] in which basis functions are represented in scalar basis and

unphysical solutions are removed by diagonalizing the free particle Hamiltonian. This generates the electronic and positronic solution in 1:1 manner. We have done five different sets of calculation using five different basis sets for Sr and F. These are cc-pVDZ, aug-cc-pVTZ, aug-cc-pCVTZ, d-aug-cc-pCVTZ and aug-cc-pCVQZ for F atom [18] and dyall.v2z, dyall.v3z, dyall.cv3z, d-aug-dyall.cv3z and dyall.cv4z for Sr atom [19]. Both large and small component basis are taken in uncontracted form. None of the electrons are frozen in our correlation calculation and the virtual orbitals whose energies are greater than a certain threshold are not considered as the high energy virtual orbitals contribute less in correlation calculation.

We have taken the following strategies to code the Z-vector method. First, the one electron and two electron matrix elements are obtained from DIRAC10 package [15]. Then we have solved the NCC part i.e., the T_1 and T_2 amplitude equations. This is followed by the construction of different types of \bar{H} ($\bar{H} = (He^T)_C$). After that \bar{H} vertices are contracted with one Λ_1 or Λ_2 vertex to construct the Λ_1 and Λ_2 amplitude equations. At the end T_1 , T_2 , Λ_1 and Λ_2 amplitudes are contracted with property integrals to get corresponding property value. To solve the T_1 and T_2 amplitudes and to construct the \bar{H} , we have used a recursive intermediate factorization of diagrams as described by Bartlett and coworkers [20]. This saves enormous computational cost. To debug this code, we benchmarked our correlation energy with the results obtained from DIRAC10 with same basis, same convergence criteria and using same direct inversion in the iterative subspace (DIIS). We have achieved 7 to 8 decimal place agreement with DIRAC10 for correlation energy independent of the choice of molecules as well as of the basis sets. The discrepancy beyond this limit could be due to the use of cutoff in storing of the intermediate diagrams or the use of different convergence algorithm. The H and \bar{H} matrix elements are stored by setting a cutoff of 10^{-12} to save storage requirement as the contribution of the two body matrix elements beyond that limit is negligible. The tolerance used for the convergence of both T and Λ amplitudes is 10^{-9} . We have used the experimental bond length (2.075 Å) of SrF [21] in all the calculations.

In Table I, we present the sets of basis used in our calculations and each combination is denoted by an English alphabet letter. The fourth and fifth column of Table I represent the cutoff used and the number of spinor generated using that cutoff for correlation calculation, respectively. We also compiled the correlation energy of SrF obtained from CCSD and second-order many body perturbation theory (MBPT(2)), which uses a first-order perturbed wavefunction.

In Table II, we present the molecular dipole moment in Debye of the ground state of SrF molecule in five different basis sets. The experimental value [22] is also presented in the same table for comparison. It is clear from the table that with increase in the number of basis function the dipole moment converges towards the experimental

TABLE I: Cutoff used and correlation energy of the ground state of SrF in different basis sets

Basis			Cutoff (a.u.)	Spinor	Correlation Energy (a.u.)	
Name	Sr	F			MBPT(2)	CCSD
A	dyall.v2z	cc-pVDZ		298	-1.528622377	-1.474175309
B	dyall.v3z	aug-cc-pVTZ	500	366	-1.292096889	-1.256789931
C	dyall.cv3z	aug-cc-pCVTZ	500	436	-1.838672666	-1.775710294
D	d-aug-dyall.cv3z	d-aug-cc-pCVTZ	100	596	-1.681326043	-1.621603448
E	dyall.cv4z	aug-cc-pCVQZ	50	520	-1.454995437	-1.402836367

value. This is expected as more basis functions generate more correlation space and thereby improve the dipole moment. In particular, our calculated dipole moment in basis E is very close ($\sim 0.5\%$) to the experimental value. The results obtained for the dipole moment of

TABLE II: Molecular dipole moment (in Debye) of the ground state of SrF

Basis	Z-vector	Experiment [22]
A	3.0158	
B	3.3898	
C	3.4023	3.4676(10)
D	3.4376	
E	3.4504	

TABLE III: Comparison of molecular dipole moment of the ground state of SrF in different methods

Method	Reference	Dipole (D)
Ionic model	Torring <i>et al.</i> [23]	3.67
SCF	Langhoff <i>et al.</i> [24]	2.579
CPF	Langhoff <i>et al.</i> [24]	3.199
CISD	Langhoff <i>et al.</i> [24]	2.523
EPM	Mestdagh <i>et al.</i> [25]	3.6
HF (finite difference)	Kobus <i>et al.</i> [26]	2.5759
CCSD	Prasanna <i>et al.</i> [27]	3.41
Z-vector	This work(E)	3.4504
Expt.	Ernst <i>et al.</i> [22]	3.4676(10)

the ground state of SrF by other methods and experiment are compiled in Table III. The dipole moment of SrF was first calculated by Torring *et al.* [23] by using an ionic model and they got a value of 3.67 D. Langhoff *et al.* [24] performed the first *ab initio* calculation of the dipole moment of SrF by using Slater type of basis function. They reported the dipole moment using three different methods, i.e., self consistent field (SCF), configuration interaction in single and double approximation (CISD) and the coupled pair function (CPF) method. Among them, CISD method is not size extensive while CPF is, thus

CPF approach gives better agreement with experiment. However, Langhoff *et al.* did not consider the relativistic motion of electrons. Mestdagh *et al.*, [25] used electrostatic polarization model and got 3.6 D as a molecular dipole moment of SrF. Kobus *et al.*, [26] obtained a dipole moment of 2.5759 D by using finite difference method in the Hartree-Fock (HF) level. The first relativistic calculation of dipole moment of SrF in the CCSD model was calculated by Prasanna *et al.*, [27] by taking expectation value of the corresponding operator. The expectation value framework leads to a connected yet nonterminating series. Prasanna *et al.*, took only the linear terms in the property calculations using CCSD wavefunction and got 3.41 D as a result. Our four component Z-vector calculation gives a result of 3.4504 D by using dyall.cv4z basis for Sr [19] and aug-cc-pCVQZ basis for F [19] (basis E) and this result shows the best agreement with the experiment so far.

In Table IV, we present the parallel component of the magnetic HFS constant of ^{87}Sr and ^{19}F of the ground state of SrF molecule. We also present the experimental value [28] of those in the same table for comparison. Our calculated result using Z-vector method show good agreement with the experimental result. The highest and lowest deviation from experimental values for parallel magnetic HFS constant of ^{87}Sr atom are for the A (~ 45 MHz) and C (~ 24 MHz) basis respectively. For the parallel magnetic HFS constant of ^{19}F , the maximum and minimum deviation occur for the basis D (~ 10 MHz) and A (~ 4 MHz) basis.

The calculated magnetic HFS constant values are in good agreement with the sophisticated experiment but the extent of accuracy is not so in comparison to that of the calculated dipole moment values. This could possibly be due to the fact that as we proceed from basis A to E, we have added extra Gaussian type orbitals (GTOs) of higher angular momentum in addition to lower angular momentum. As the higher angular momentum GTO shifts the electron density towards the outer region, the addition of higher angular momentum GTO improves the outer region much better than the inner region of the molecular wavefunction. This is why as we go from basis A to E, our molecular dipole moment value matches more closely than the magnetic HFS values with the experimental results.

TABLE IV: Parallel (A_{\parallel}) magnetic hyperfine structure constant of the ground state of SrF in MHz

Basis	^{87}Sr		^{19}F	
	Z-vector	Experiment [28]	Z-vector	Experiment [28]
A	546.08		121.93	
B	558.96		118.70	
C	566.62	591(3)	119.64	126(3)
D	561.25		116.35	
E	559.65		117.74	

We have successfully implemented Z-vector method in the relativistic NCC domain using 4-component wave function to calculate the first order energy derivatives. We applied this method to calculate the molecular dipole moment and parallel magnetic HFS constant of SrF molecule. The results from our calculations are in good agreement with the experimental values. Therefore, we

can conclude that Z-vector method in the relativistic framework can produce an accurate wavefunction in the near nuclear region as well as far from the nucleus.

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